Case HF/1-22727

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

IN RE PCT NATIONAL STAGE APPLICATION OF
PIERRE DREYER ET AL
INTERNATIONAL APPLICATION NO. PCT/EP 03/09409
FILED: AUGUST 26, 2003
FOR: FORMULATIONS COMPRISING WATER-SOLUBLE GRANULATES
U.S. APPLICATION NO: 10/526,093
35 USC 371 DATE: FEBRUARY 23, 2005

Group Art Unit 1796
Examiner: G.R.Delcotto

DECLARATION UNDER RULE 132

I, ULLRICH MENGE, a citizen of Germany, residing at 45, Schlossgasse, 79639 Grenzach-Wyhlen, Germany, hereby declare:

That I was awarded the degree of a Dipl. Chemist, Technical University Berlin, Germany, in 1994;

That I have been employed by Ciba as a chemist since 2000 and presently hold the position of the Head of Product Formulations for Home & Personal Care in the Segment Plastic Additives;

That I have been engaged in the field of Home & Fabric Care for Ciba since 2000;

That based on the above education and experience, I consider myself an expert in the field of Fabric Care (detergents and rinse conditioners).

I, ULLRICH MENGE, declare that the preparation of the Formulations A, B, C, D, E and F as indicated in Part I of this Declaration as well as the following determination of the rate of dissolving in water and the resistance in nonionic surfactants of the granulates tested indicated in Part II of this Declaration were carried out under my direction and supervision;

That I am submitting herewith the following exact report of the preparations and tests mentioned below.

I, ULLRICH MENGE, declare that the following tests were carried out under my direction and supervision. That I am submitting herewith the following exact report of the tests and the results obtained.

Part I

Formulation

The formulations compared were selected according to closest similarity.

The Formulation A was prepared in analogy to the prescription given in US Patent No. 6,291,412, Example 10 in column 17.
The granules from this example are comparable in composition to Example 1 in column 14 of the instant patent application, only that the drying method is different (fluidized bed spray drying in Example 10 of US Patent No. 6,291,412, and spray drying in Example 1 of the instant Patent Application No. 10/526,093 (PCT/EP2003/009409)).

The Formulation B was prepared according to the prescription given in the instant U.S. Patent Application No. 10/526,093 (PCT/EP2003/009409) in Example 11 for the preparation of the phthalocyanine solution and in Example 44 for the preparation of the granulate (with fluidized bed spray drying).
To achieve closest similarity to Formulation A, the composition was adjusted in such a way that the final product contains 10% per weight of the Zn-phthalocyanin sulfonate and 48% of the disperging agent (condensation product of formaldehyde with naphthalenesulfonic acid) used in Formulation A. The remainder is 37% of sodium sulphate and 5% water.

The Formulation C was prepared according to the prescription given in the instant U.S. Patent Application No. 10/526,093 (PCT/EP2003/009409) in the Example 6 for the preparation of the phthalocyanine solution and in Example 49 for the preparation of the granulate (with fluidized bed spray drying).
Formulation C contains a mixture of aluminium phthalocyanin and zinc phthalocyanin sulfonates. Disperging agent is the same as in Formulations A and B.

The Formulation D was prepared according to the prescription given in the instant U.S. Patent Application No. 10/526,093 (PCT/EP2003/009409) in the Example 21 for the preparation of the phthalocyanine solution. The mixture was oven-dried and then comminuted in a laboratory mixer, as outlined on page 33.
The resulting solid product contains 9% per weight of the aluminium and zinc phthalocyanin sulfonates, 55% of disperging agents, 27% of salt, 3% of zeolite, and 6% of water.

The Formulation E was prepared according to the prescription given in the instant U.S. Patent Application No. 10/526,093 (PCT/EP2003/009409) in the Example 15 for the preparation of the phthalocyanine solution. The mixture was oven-dried and then comminuted in a laboratory mixer, as outlined on page 33.
The resulting solid product contains 17% per weight of the aluminium and zinc phthalocyanin sulfonates, 11% of polymer, 68% of sodium sulphate and 4% of water.

The Formulation F was prepared in analogy to the prescription given in the instant U.S. Patent Application No. 10/526,093 (PCT/EP2003/009409) in Example 11 for the preparation of the phthalocyanine solution and in Example 44 for the preparation of the granulate (with fluidized bed spray drying) with the exception of not using a dispersing agent.
In analogy to Formulation A, the composition was adjusted in such a way that the final product contains 10% per weight of the Zn-phthalocyanin sulfonate. The remainder is 89%

sodium sulphate and less than 1% water. This Formulation F did not contain any dispersing agent.

Part II

For the evaluation of the formulations, the rate of dissolution in water and the solubility in liquid nonionic surfactant were determined. The significance of these properties for the application is explained in detail in US Patent No. 4,990,280, column 1, lines 12 to 47, lines 54 and 55 and in column 2, lines 43 to 57.

I) Quantitative Determination of Water Solubility

1000 ml of deionised water were provided in a 1200 ml glass beaker. The pH value was adjusted to 9.5 with borax. A metal stirrer having a diameter of 5.5 cm was arranged in such a way that the head of the stirrer has a distance of 4 cm from the bottom of the glass beaker. The stirrer is running with 50 r.p.m. The temperature is room temperature. 50 mg of the granulate (Formulation A, B, C, D or E, respectively) are put at once on to the water surface in the mid between the stirrer staff and the side of the glass beaker (the time was set as t = 0). At this slow stirrer speed, the granules did not evenly distribute in the water volume and were much less present in the volume close to the glass wall. The water was increasingly coloured while granulate was dissolving, and a levelling of the colouration over the whole volume was observed with time. At the particular time after 30, 60, 120, 180 and 300 seconds (t = 30, t = 60, t = 120 and t = 180 and t = 300), 4 ml of the solution was taken out at a point located close to the glass beaker wall and transfered into a cuvette. The solution were measured and compared with pure water. The measurement was done at 669 nm which is the maximum of absorbance of the photo catalyst and in a cuvette having an optical density of 1 cm. The baseline of the spectrophotometer was done with pure water. The granulate was completely dissolved after 300 seconds and the colour was uniformly in the whole glass beaker. The ratio of dissolved granulate was compared to the final value after 300 seconds according to the following scheme:

$$\text{ratio of dissolved granulate in \% after t seconds} = \frac{\text{extinction after t seconds}}{\text{extinction after 300 seconds}}$$

Three trials were done with all samples and the average taken for each sample.

II) Comparison of the rate of dissolving in water of the granulates tested

Table 1

Formulation used	% dissolved after t = 30, 60, 120 and 180 seconds			
	30	60	120	180
A	80	95	99.9	100
B	93	98	100	100
C	97	99.5	100	100
D	94	98.5	99.9	100
E	90	99	100	100

As evident from the Table 1, the Formulations B, C, D and E are superior to the closest formulation of the prior art (Formulation A) as given in Part I with regard to the rate of dissolving in water.
The known formulation A does not reach the rate of dissolving in water obtainable with formulations B, C, D and E.

III) Quantitative determination of solubility in liquid nonionic surfactant

In a 50 ml flask, 25mg of the granule were introduced into 25g of melted nonionic surfactant (Neodol 45-7E, from Shell) and then kept at 40°C for one hour while gently stirring. Then the mixture was filtered into a cuvette and measured and compared with the nonionic surfactant as a reference. The measurement was done at 669 nm which is the maximum of absorbance of the photo catalyst and in a cuvette having an optical density of 1 cm. The baseline of the spectrophotometer was done with pure nonionic surfactant. All solutions were kept at 40°C prior to the measurement.

IV) Comparison of the solubility in liquid nonionic surfactant of the granulates tested

Table 2

Formulation used	Absorbance measured at 669nm
A	0,008
B	0,009
F	0,320

As evident from the Table 2, the Formulations B was comparable to the closest formulation of the prior art (Formulation A) as given in Part I with regard to the solubility in nonionic surfactants.
The Formulation F (salt based granule without dispersing agent or polymer) much stronger dissolved in nonionic surfactant as was evident from the high extinction value. US Patent No. 4,990,280 teaches that such a granule cannot be used in relevant detergents. This is evident as the photocatalyst active is strong in color, and photocatalyst granules are often used in white (non-colored) detergents. A significant leakage of photocatalyst into the detergent matrix will lead to a noticable discoloration of the product during storage which is not acceptable for the end consumer.

As a conclusion of the performed tests, the Formulations B, C, D and E were superior to prior art Formulation A as they combine the advantage of a higher dissolution rate in water with the same high level of stability in nonionic surfactants. Consequently, the granules of the instant patent application have a lower risk of spotting in the laundry application while maintaining the good storage stability in the final detergent powder.

Part III

I, ULLRICH MENGE, hereby declare:

1. That based on my education and experience, I consider myself an expert in the field of Fabric Care;
2. That the results of the above tests show that the Formulations B, C, D and E according to the instant invention are superior to the closest Formulation A of the prior art with respect to the property tested (rate of dissolving of granules in water and dissolution in nonionic surfactant);
3. The rate of dissolving in water is an important feature for the industry and an improvement in this property is of considerable importance because problems often arise if photoactivators dissolve too slowly in water, especially when there is inadequate mixing of the washing liquor, because the coloured photoactivators stain the laundry, and thus the washings become spotted. At the same time, there is the need for stability of the granules in the final product to prevent discoloration of the detergent powder, which is related to the high solubility of the phthalocyanin sulfonate in nonionic surfactants;
4. That the above given measurement degree of the rate of dissolving of granules demonstrates a significant improvement in this property which is of commercial importance;
5. That the improvement attainable with respect to degree of the rate of dissolving of granules and at the same time maintaining the stability in nonionic surfactants at high salt levels of the granule could not be foreseen and the results of the tests are surprising to me and I would never have predicted such difference in the property tested.

I, ULLRICH MENGE, declare further that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that wilful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 Title 18 of the United States Code and that such wilful false statements may jeopardize the validity of the application or any patent issuing thereon.

Signed this th day of January 2008

ULLRICH MENGE